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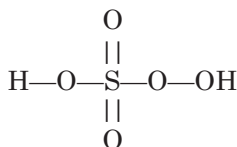
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CARO'S ACID

[7722-86-3]

Formula: H_2SO_5 ; MW 114.08;

Structure:



Synonyms: peroxymonosulfuric acid; persulfuric acid: sulfomonoperacid

Uses

Caro's acid is used in the preparation of dyes and bleaching agents. It also is used as a strong oxidizing reagent to convert ketones to lactones, to convert olefins to glycols and esters, and to analyse pyridine, aniline and many alkaloids.

Physical Properties

White crystalline solid; unstable, decomposes at 45°C ; commercial product is a syrupy liquid containing equal parts of Caro's acid and sulfuric acid; stored at dry ice temperature; very soluble in water.

Preparation

Caro's acid may be prepared by several methods depending on what form of the reagent is desired. Most commonly, it is made by treating potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) with sulfuric acid. The dry form is prepared by slowly stirring 100 g $\text{K}_2\text{S}_2\text{O}_8$ into 60 mL of concentrated H_2SO_4 , followed by adding 300 g potassium sulfate. A liquid Caro's acid is obtained by slowly stirring $\text{K}_2\text{S}_2\text{O}_8$ into three times the mass of H_2SO_4 . The dilute form of the reagent may be obtained by either mixing $\text{K}_2\text{S}_2\text{O}_8$ to 40% H_2SO_4 or by treating $\text{K}_2\text{S}_2\text{O}_8$ with H_2SO_4 and adding ice to the mixture.

Alternatively, Caro's acid may be prepared from hydrogen peroxide by treatment with either chlorosulfonic acid or with H_2SO_4 at -40°C . A 90% H_2O_2 is used in the preparation.

Caro's acid is a strong oxidizing agent and is very unstable. All laboratory preparations must be carried out in an explosion-proof fume hood under temperature-controlled conditions and in the absence of impurities and oxidizable substances.

Hazard

Many accidents have been reported involving the preparation and the use of this compound. The compound is sensitive to heat and shock. Reactions with organic matter, finely divided metals and other readily oxidizable substances can be violent to explosive. It is a strong irritant to skin, eyes and mucous membranes.

CERIC AMMONIUM NITRATE

[16774-21-3]

Formula: $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$; MW 548.22

Synonyms: ammonium ceric nitrate; ammonium hexanitratocerate (IV)

Uses

Ceric ammonium nitrate is used as a volumetric oxidizing reagent in many oxidation-reduction titrations. Cerium(IV) ion is a strong oxidant similar to permanganate ion. It is the most widely-used primary standard among all Ce(IV) compounds. Other applications of this compound are in organic oxidation reactions; and as a catalyst in polymerization of olefins.

Physical Properties

Reddish-orange monoclinic crystals; very soluble in water.

Preparation

Ceric ammonium nitrate is prepared by electrolytic oxidation of cerous nitrate in nitric acid to ceric nitrate, followed by the addition of ammonium nitrate solution. It is separated from the solution by crystallization. It may be prepared alternatively by dissolving cerium(II) oxide, $\text{CeO} \cdot \text{H}_2\text{O}$ in concentrated nitric acid followed by treatment with ammonium nitrate.

Reactions

The most important reactions of this compound are the oxidations, attributed to Ce^{4+} ion in the solution. The standard reduction potential E° for the formal half-reaction: $\text{Ce}^{4+} + e^- \longleftrightarrow \text{Ce}^{3+}$ in 1 M H_2SO_4 is 1.44 V. The oxidizing strength is comparable to permanganate (MnO_4^-), bromate (BrO_3^-), and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anions. Analytical applications involve reactions with reductants such as sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) or arsenic (III) oxide (As_2O_3) in the presence of iron, with ferroin (1,10-phenanthroline iron(II) complex) as the indicator.

Analysis

Elemental composition: Ce 25.56%, H 1.47%, N 20.44%, O 52.53%. The aqueous solution of the compound may be analyzed for Ce by AA or ICP spectrophotometry. Also, the solution may be measured for NH_4^+ ion by ammonium ion-selective electrode and the NO_3^- ion by nitrate ion-specific electrode, ion chromatography or cadmium-reduction colorimetry. For all these measurements, the solution may require sufficient dilutions. For quantitation, its solution may be standardized by titration with a reducing agent such as sodium oxalate in the presence of iron and ferroin indicator.

Hazard

The compound is a powerful oxidizing agent. Precautions should be taken to avoid accidental contacts with organic or other readily oxidizable substances.

CERIUM

[7440-45-1]

Symbol: Ce; atomic number 58; atomic weight 140.115; a rare-earth metal; a lanthanide series inner-transition *f*-block element; metallic radius (alpha form) 1.8247Å(CN=12); atomic volume 20.696 cm³/mol; electronic configuration [Xe]4f¹5d¹6s²; common valence states +3 and +4; four stable isotopes; Ce-140 and Ce-142 are the two major ones, their percent abundances 88.48% and 11.07%, respectively. Ce-138 (0.25%) and Ce-136(0.193%) are minor isotopes; several artificial radioactive isotopes including Ce-144, a major fission product (*t*_{1/2} 284.5 days), are known.

Occurrence and Uses

The element was discovered by Klaproth in 1803 and also in the same year by Berzelius and Hisinger. It is named after the asteroid Ceres. Cerium is found in several minerals often associated with thorium and lanthanum. Some important minerals are monazite, allanite, cerite, bastnasite, and samarskite. It is the most abundant element among all rare-earth metals. Its abundance in the earth's crust is estimated to be 66 mg/kg, while its concentration in sea water is approximately 0.0012 microgram/L.

The compounds of cerium have many important industrial applications, especially in the glass industry, or as catalysts (see under individual compounds). The metal itself has many uses.

Misch metal, an alloy of cerium with other lanthanides is a pyrophoric substance and is used to make gas lighters and ignition devices. Some other applications of the metal or its alloys are in solid state devices; rocket propellant compositions; as getter in vacuum tubes; and as a diluent for plutonium in nuclear fuel.

Physical Properties

Greyish lustrous metal; malleable; exhibits four allotropic modifications: the common γ -form that occurs at ordinary temperatures and atmospheric pressure, β -form at -16°C, α -form below -172°C, and δ -form at elevated temperatures above 725°C; crystal structure—face-centered cubic type (γ -Ce); density 6.77 g/cm³; melts at 799°C; vaporizes at 3,434°C; electrical resistivity 130 microhm.cm (at the melting point); reacts with water.

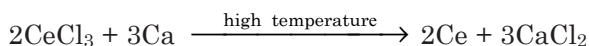
Thermochemical Properties

ΔH° (cry)	0.0
ΔH° (g)	101.1 kcal/mol
ΔG_f° (g)	92.02 kcal/mol
S° (cry)	17.21 cal/degree mol
S° (g)	45.84 cal/degree mol
C_p (cry)	6.43 cal/degree mol
C_p (g)	5.52 cal/degree mol
ΔH_{fus}	1.30 kcal/mol

Production

Cerium is obtained from its ores by chemical processing and separation. The process involves separation of cerium from other rare-earth metals present in the ore. The ore is crushed, ground, and treated with acid. The extract solution is buffered to pH 3–4 and the element is precipitated selectively as Ce^{4+} salt. Cerium also may be separated from other metals by an ion-exchange process.

Also, the metal may be obtained by high temperature reduction of cerium(III) chloride with calcium:

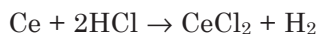


Reactions

The chemical properties of cerium, like all other elements, are governed largely by the electrons in its outermost shells. In the rare earth elements, the energies of $4f$, $5d$, and $6s$ orbitals are very close. Cerium, which has two $6s$, one $5d$ and one $4f$ electrons can, therefore, exhibit the oxidation states of either +3 or +4 by the loss of either two s and one d electrons or an additional one f electron, respectively. Some examples of Ce^{3+} (cerous) compounds are Ce_2O_3 , $\text{Ce}(\text{OH})_3$, $\text{Ce}_2(\text{SO}_4)_3$, Ce_2S_3 , $\text{Ce}(\text{NO}_3)_3$ and $\text{Ce}_2(\text{CO}_3)_3$. Similarly, it forms many ceric compounds in +4 oxidation state, such as CeO_2 , $\text{Ce}(\text{SO}_4)_2$, CeCl_4 and CeF_4 . Compounds in +2 oxidation states are also known. These include CeH_2 , CeS and CeI_2 .

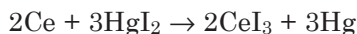
The metal is stable in dry air at ordinary temperatures. Upon heating, it converts to ceric oxide, CeO_2 . The finely divided metal may ignite spontaneously. It is oxidized in moist air at ambient temperatures. It reacts with water forming cerium(III) hydroxide.

Reactions with dilute mineral acids yield the corresponding salts:



It forms cerium(II) hydride, CeH_2 , when heated under hydrogen. Reaction with H_2S yields cerium sulfide, Ce_2S_3 .

The standard redox potential of the reaction $\text{Ce}^{3+} + 3\text{e}^- \rightarrow \text{Ce}$ is -2.2336 V. The metal undergoes single replacement reactions, displacing less electropositive metals from their salts in solution or melt:



Analysis

Cerium may be analyzed in solution by AA or ICP techniques. The metal or its compounds are digested in nitric acid, diluted appropriately prior to analysis. Also, it may be measured by ICP/MS at a still lower detection level (low ppt). The metal may be analyzed nondestructively by x-ray techniques.

CERIUM(III) CHLORIDE

[7790–86–5]

Formula: CeCl_3 ; MW 246.47; forms heptahydrate, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, [18618–55–8]

Synonym: cerous chloride

Uses

Cerium(III) chloride is used to prepare cerium metal and other cerium salts. It also is used as a catalyst in olefin polymerization, and in incandescent gas mantles.

Physical Properties

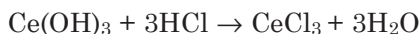
White, very fine powder; hexagonal crystal system; heptahydrate is yellow orthogonal crystal and hygroscopic; density of anhydrous salt 3.97 g/cm^3 ; melts at 817°C ; vaporizes at $1,727^\circ\text{C}$; heptahydrate begins to lose water above 90°C and becomes anhydrous at about 230°C ; soluble in water and alcohol; hexahydrate has greater solubility in these solvents.

Thermochemical Properties

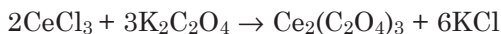
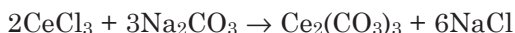
ΔH_f°	–251.79 kcal/mol
ΔG_f°	–233.70 kcal/mol
S°	36.90 cal/degree mol
C_p	20.89 cal/degree mol

Production

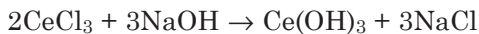
Cerium(III) chloride is prepared by the reaction of hydrochloric acid with a cerium salt, such as cerium hydroxide or carbonate, followed by crystallization;

**Reactions**

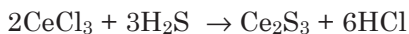
Cerium chloride in aqueous phase would undergo double decomposition reactions with many soluble salts of other metals; e.g.:



Reactions with caustic alkalis yield cerous hydroxide:



When H_2S is passed into the solution cerium sulfide is precipitated:



Analysis

Elemental composition: Ce 56.85%, Cl 43.15%. In the aqueous phase following acid digestion, cerium may be analyzed by various instrumental techniques (see Cerium). Chloride ion in the solution may be measured by ion chromatography, chloride ion-selective electrode or titration with silver nitrate using potassium chromate indicator. The solution may require appropriate dilution for analysis of both the metal and the chloride anion.

CERIUM(III) HYDROXIDE

[15785–09–8]

Formula: $\text{Ce}(\text{OH})_3$; MW 191.14

Synonyms: cerous hydroxide; cerium hydroxide; cerous hydrate

Uses

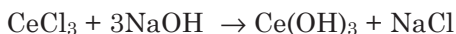
The pure compound is used in glazes and enamels as an opacifying agent. It also is used to make colored glass, imparting yellow color to the glass. The crude form is used in flaming arc lamps. Another application of this compound is in the preparation of several other cerium salts.

Physical Properties

White gelatinous precipitate; decomposes on heating, forming oxide; soluble in acids and ammonium carbonate solution; insoluble in alkalis.

Preparation

Cerium(III) hydroxide is obtained in industrial scale from monazite sand, $(\text{Ce}, \text{La}, \text{Th})\text{PO}_4$. In the laboratory, it may be prepared by treating caustic soda solution with cerium(III) chloride, followed by crystallization.

**Analysis**

Elemental composition: Ce 73.30%, H 1.58%, O 25.11%. The compound may be analyzed for Ce in aqueous phase by AA or ICP spectrophotometry after it is digested with nitric acid and diluted appropriately.

CERIUM(III) NITRATE

[10108–73–3]

Formula: $\text{Ce}(\text{NO}_3)_3$; MW 326.15; also forms tri-, tetra- and hexahydrates; the hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is most stable.

Synonym: cerous nitrate

Uses

Cerium(III) nitrate is used for the separation of cerium from other rare-earth elements. It also is used as a catalyst in hydrolysis of phosphoric acid esters.

Physical Properties

Hexahydrate is a colorless crystal; hygroscopic; loses water on heating—three molecules of water of crystallization expelled at 150°C; decomposes at 200°C; readily dissolves in water, alcohol, and acetone.

Thermochemical Properties

ΔH_f° (Ce(NO ₃) ₃)	−293.0 kcal/mol
ΔH_f° (Ce(NO ₃) ₃ • 3H ₂ O)	−516.0 kcal/mol
ΔH_f° (Ce(NO ₃) ₃ • 4H ₂ O)	−588.9 kcal/mol
ΔH_f° (Ce(NO ₃) ₃ • 6H ₂ O)	−729.1 kcal/mol

Preparation

Cerium(III) nitrate may be prepared by the action of nitric acid on a cerium(III) salt, followed by crystallization:

**Analysis**

Elemental composition: Ce 42.96%, N 12.88%, O 44.15%. The aqueous solution of this water-soluble compound may be analyzed directly for Ce (without any acid digestion) by AA or ICP spectrophotometry, and for the nitrate ion by ion chromatography or nitrate ion-selective electrode. The solution may require sufficient dilution for analysis.

CERIUM(IV) OXIDE

[1306–38–3]

Formula: CeO₂; MW 172.11

Synonyms: ceria; ceric oxide

Uses

Cerium(IV) oxide is used in the glass industry as an abrasive for polishing glass and as an opacifier in photochromic glass. It inhibits discoloration of glass made for shielding radiation. It also is used in ceramic coatings, enamels, and refractory materials. Other applications of this compound are in semiconductors, cathodes, capacitors, and phosphors; as a diluent in nuclear fuels; as a catalyst in organic synthesis; and in oxidimetry for analyzing cerium.

Physical Properties

White powder in pure form; technical grade material is pale yellow; pres-

204 CERIUM(IV) SULFATE

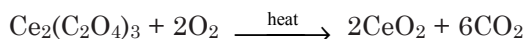
ence of other lanthanide elements as impurities may impart reddish color; cubic crystal; density 7.65 g/cm³; melts at 2,400°C; insoluble in water.

Thermochemical Properties

ΔH_f°	-269.21 kcal/mol
ΔG_f°	-244.89 kcal/mol
S°	14.89 cal/degree mol
C_p	14.72 cal/degree mol

Preparation

Cerium(IV) oxide may be obtained by heating cerium oxalate, carbonate or other salts at elevated temperatures:



Analysis

Elemental composition: Ce 81.41%, O 18.59%. The oxide can be determined by x-ray techniques. The compound may be digested with HNO₃—HCl mixture, the acid extract diluted appropriately and analyzed by AA or ICP spectrophotometry (see Cerium).

CERIUM(IV) SULFATE

[13590-82-4]

Formula: Ce(SO₄)₂; MW 332.35; also forms a tetrahydrate, Ce(SO₄)·4H₂O

[10294-42-5]

Synonym: ceric sulfate

Uses

Cerium(IV) sulfate is used in radiation dosimeters and as an oxidizing agent in volumetric analysis. The tetrahydrate is used in dyeing and printing textiles, and in waterproofing.

Physical Properties

White crystalline powder; orthogonal crystal system; the tetrahydrate is a yellow-to-orange powder which, on heating at 180°C, loses all molecules of water; density of tetrahydrate 3.91 g/cm³; anhydrous salt decomposes at 350°C forming CeOSO₄; soluble in water (decomposes); soluble in dilute H₂SO₄ and other concentrated mineral acids.

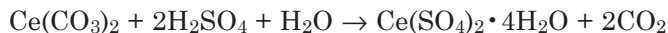
Thermochemical Properties

ΔH_f° (aq)	-595.9 kcal/mol
ΔG_f° (aq)	-523.6 kcal/mol

Preparation

Cerium(IV) sulfate is prepared by heating cerium(IV) oxide, CeO₂ with con-

centrated H_2SO_4 . Also it may be obtained by the reaction of H_2SO_4 with cerium carbonate:



Analysis

Elemental composition: Ce 42.18%, S 19.30%, O 38.53%. It is digested with nitric acid, diluted appropriately and analyzed for Ce by AA or ICP spectroscopy (see Cerium). The compound may be dissolved in small quantities of water (forms a basic salt when treated with large a volume of water). The solution is analyzed for sulfate ion by gravimetry following precipitation with barium chloride. Alternatively, the compound is dissolved in hot nitric acid and the solution analyzed for sulfate by ion-chromatography.

CESIUM

[7440-46-2]

Symbol Cs; atomic number 55; atomic weight 132.905; a Group IA (Group 1) alkali metal element; electron configuration $[\text{Xe}]6s^1$; atomic radius 2.65 Å; ionic radius (Cs^+) 1.84 Å; ionization potential 3.89 eV; valence +1; natural isotope Cs-133; 37 artificial isotopes ranging in mass numbers from 112 to 148 and half-lives 17 microseconds (Cs-113) to 2.3×10^6 years (Cs-135).

Occurrence and Uses

Cesium was discovered by Bunsen and Kirchoff in 1860. It is found in the minerals pollucite, lepidolite, and the borate rhodizite. Pollucite, $\text{CsAlSi}_2\text{O}_6$, is a hydrated silicate of aluminum and cesium. The concentration of cesium in the earth's crust is estimated to be 3 mg/kg, and in sea water 0.3 µg/L.

Cesium is used as a getter in electron tubes. Other applications are in photoelectric cells; ion propulsion systems; heat transfer fluid in power generators; and atomic clocks. The radioactive Cs-137 has prospective applications in sterilization of wheat, flour, and potatoes.

Physical Properties

Golden yellow, soft and ductile metal; body-centered cubic structure; density 1.93 g/cm³; melts at 28.44°C; vaporizes at 671°C; vapor pressure 1 torr at 280°C; electrical resistivity 36.6 microhm-cm (at 30°C); reacts with water; dissolves in liquid ammonia forming a blue solution.

Thermochemical Properties

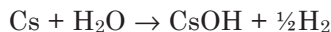
ΔH_f° (cry)	0.0
ΔH_f° (gas)	18.28 kcal/mol
ΔG_f° (gas)	11.85 kcal/mol
S° (cry)	20.36 cal/degree mol
S° (gas)	41.97 cal/degree mol
C_p (cry)	7.70 cal/degree mol
ΔH_{fus}	0.502 kcal/mol

Production

Cesium is obtained from its ore pollucite. The element in pure form may be prepared by several methods: (i) electrolysis of fused cesium cyanide, (ii) thermal reduction of cesium chloride with calcium at elevated temperatures, and (iii) thermal decomposition of cesium azide. It is stored under mineral oil. The element must be handled under argon atmosphere.

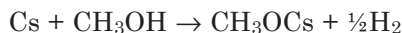
Reactions

Cesium is highly reactive. It is the most electropositive metal—more electropositive and reactive than other alkali metals of lower atomic numbers. The standard redox potential E° for the reduction $\text{Cs}^+ + e^- \rightarrow \text{Cs}$ is -3.026 V . It reacts explosively with water, forming cesium hydroxide, CsOH and hydrogen:



Combustion with oxygen (or air) first forms oxide, Cs_2O , which converts to the peroxide, Cs_2O_2 , and then superoxide, CsO_2 . Peroxide and superoxide are also formed by passing a stoichiometric amount of oxygen in the solution of cesium in liquid ammonia. Cesium is also known to form highly colored suboxides such as Cs_{11}O_3 which look metallic.

Cesium combines with most nonmetals forming one or more binary compounds. With sulfur, it forms ionic sulfides, such as Cs_2S , CsS_4 and Cs_2S_6 . It reacts violently with halogens forming the corresponding halides. Reaction with nitrogen yields cesium nitride Cs_3N . Heating with carbon produces interstitial compounds of nonstoichiometric compositions. Cesium dissolves in alcohols forming cesium alkoxides with liberation of hydrogen.



Complex alkoxides of the type $[\text{CsOR}]_n$ are known, structures of which have not been well defined. It reacts with amines forming amido complexes of the type CsNHR or CsNR_2 . The structures of crystalline complexes are complicated, depending upon the solvent and other factors.

Analysis

Cesium can be analyzed by various instrumental techniques including atomic absorption and atomic emission spectrophotometry and various x-ray methods. The most sensitive wavelength for AA measurement is 852.1 nm . It imparts a reddish violet color to flame. It is identified by specific line spectra having two bright lines in the blue region and several other lines in the red, yellow, and green.

Hazard

Cesium is a pyrophoric metal. It ignites spontaneously in air or oxygen. It reacts violently with cold water evolving hydrogen. Similar violent reactions occur with anhydrous acids and halogens.

CESIUM CHLORIDE

[7647-17-8]

Formula: CsCl; MW 168.36

Uses

Cesium chloride is used in radio and television vacuum tubes. It also is used in ultracentrifuge separations; x-ray fluorescent screens; as radiographic contrast medium, and to prepare cesium and other cesium salts.

Physical Properties

White cubic crystal; hygroscopic; density 3.99 g/cm³; melts at 645°C; vaporizes at 1297°C; very soluble in water, soluble in ethanol.

Thermochemical Properties

ΔH_f°	-105.88 kcal/mol
ΔG_f°	-99.07 kcal/mol
S°	24.19 cal/degree mol
C_p	12.55 cal/degree mol
ΔH_{fus}	3.80 kcal/mol

Preparation

Cesium chloride is prepared by the treatment of cesium oxide or any cesium salt with hydrochloric acid followed by evaporation and crystallization of the solution.

Analysis

Elemental composition: Cs 78.94%, Cl 21.06%. An aqueous solution may be analyzed for the element Cs by atomic absorption or emission spectroscopy and chloride by ion chromatography, chloride ion-selective electrode, or by titration with a standard solution of silver nitrate or mercuric nitrate.

CESIUM HYDROXIDE

[21351-79-1]

Formula: CsOH; MW 149.91

Synonym: cesium hydrate

Uses

Cesium hydroxide is used as electrolyte in alkaline storage batteries. Other applications of this compound involve catalytic use in polymerization of cyclic siloxane; and treatment of hazardous wastes.

Physical Properties

White to yellowish fused crystalline mass; highly deliquescent; very alkaline; density 3.68 g/cm³; melts 272°C; highly soluble in water; soluble in

ethanol; aqueous solution is very alkaline.

Thermochemical Properties

$$\Delta H_f^\circ \quad -99.7 \text{ kcal/mol}$$

Preparation

Cesium hydroxide is prepared by electrolysis of cesium salts to obtain cesium metal, which then reacts with water to yield hydroxide. It also is prepared by the action of barium hydroxide with an aqueous solution of cesium sulfate.

Reactions

Cesium hydroxide is the strongest base known. Its aqueous solution undergoes neutralization reactions with acids. Precipitation reactions don't yield crystalline cesium salts because of their high solubility.

Analysis

Elemental composition: Cs 88.65%, H 0.67%, O 10.67%. CsOH can be standardized by acid-base titration using HCl or H₂SO₄ and a color indicator, or by potentiometric titration to neutral pH.

CHLORINE

[7782-50-5]

Symbol Cl; atomic number 17; atomic weight 35.452; a nonmetallic Group VIIA (Group 17) halogen group element; electron configuration [Ne]3s²3p⁵; most common valence -1; also oxidation states from +1 to +7 are known; electronegativity 3.0; occurs as a diatomic molecule Cl₂ containing a single covalent bond in which Cl-Cl bond distance 1.99 Å; two stable isotopes Cl-35 (75.53%) and Cl-37 (24.37%); seven radioactive isotopes.

Occurrence and Uses

Chlorine does not occur in the elemental state because of its high reactivity. In nature the element occurs mainly as sodium chloride in seawater. Its abundance in seawater is 1.9% by weight. It also exists as chloride in many rocks and minerals such as carnallite (KMgCl₃·6H₂O) and sylvite (KCl).

Chlorine was discovered by Scheele in 1774 and named by Davy in 1810. Chlorine has numerous industrial applications. Some of the most important uses of chlorine are (i) in the production of a large number of organic chloro derivatives used in processing or producing paper, textiles, paints, dyes, medicines, antiseptics, petrochemicals, pesticides, plastics, foodstuffs, solvents, and other consumer products, (ii) as a disinfectant and bactericide in water treatment and purification, (iii) as an oxidizing agent, (iv) as a substituent agent in a number of organic reactions, and (v) in making chlorinated lime (bleaching powder) for bleaching fabrics and other substances. Other uses are in food processing; shrink proofing wool; and removal of tin and zinc from iron.

Radioactive Cl-36 has a half-life 440,000 yr (β⁻ decay). It is used as a trac-

er for studying corrosion of steel by salt water; to measure chlorosubstitution mechanisms in organics; and to determine geological age of meteorites.

Physical Properties

Greenish-yellow gas; suffocating odor (odor threshold 3 ppm); gas density in the air 2.46 (air = 1); becomes a pale yellow liquid at -34.04°C ; the color decreases with lowering temperature; becomes a pale yellow crystal at -101.5°C ; critical temperature 143.8°C ; critical pressure 76.89 atm; critical volume $123\text{ cm}^3/\text{mol}$; moderately soluble in water; solubility in water $0.061\text{ mol Cl}_2/\text{L}$ at 20°C ; bulk solubility in water (including all species formed) 0.091 mol/L .

Thermochemical Properties

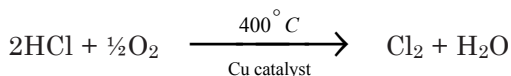
$\Delta H_f^{\circ}(\text{Cl}_2\text{ gas})$	0.0
$\Delta H_f^{\circ}(\text{Cl gas})$	28.99 kcal/mol
$\Delta G_f^{\circ}(\text{Cl gas})$	25.17 kcal/mol
$S^{\circ}(\text{Cl gas})$	39.48 cal/degree mol
$C_p(\text{Cl gas})$	5.21 cal/degree mol
ΔH_{vap}	4.88 kcal/mol
ΔH_{fus}	1.53 kcal/mol

Production

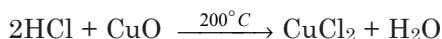
Chlorine is produced industrially by electrolysis of brine using either mercury cathode cells or, preferably, various commercially available membrane cells. Chlorine gas is liberated at the anode while sodium hydroxide and hydrogen are liberated at the cathode:

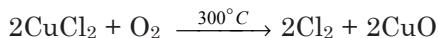


Also, Cl is made by electrolysis of fused sodium chloride, magnesium chloride salt, or hydrochloric acid. The electrolytic process has practically superseded the Weldon and Deacon processes employed earlier to produce chlorine. The Weldon process involves the action of HCl on manganese dioxide ores to produce chlorine and manganese chloride. The MnCl_2 liquor obtained is first converted into calcium manganite ($\text{CaO} \cdot 2\text{MnO}_2$) or "Weldon mud," from which MnO_2 is generated back for reuse. Deacon's process involves catalytic oxidation of hydrogen chloride, catalyzed by copper:



The efficiency of Deacon's process is improved by passing the HCl over CuO at 200°C . The product CuCl_2 is oxidized at 300°C by treatment with oxygen:





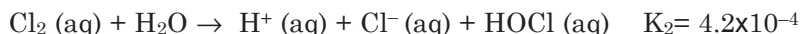
In the laboratory, chlorine may be prepared by oxidation of HCl with manganese dioxide:



Reactions

Chlorine gas is noncombustible but, like oxygen, it supports combustion. It combines with practically all elements except nitrogen and the inert gases, helium, neon, argon, krypton, and radon. A few compounds with the inert gas xenon are also known. The diatomic Cl_2 molecule can dissociate into Cl atoms upon heating or irradiation with UV.

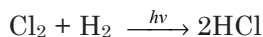
Chlorine is moderately soluble in water forming an equilibrium between dissolved chlorine and hypochlorous acid in the aqueous solution:



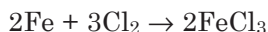
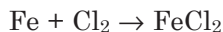
The concentration of hypochlorous acid in a saturated solution of chlorine in water at 25°C is 0.030 mol/L while dissolved chlorine, $\text{Cl}_2 (\text{aq})$ is 0.061 mol/L (Cotton, F. A., G. Wilkinson, C. A. Murillo and M. Bochmann. 1999. *Advanced Inorganic Chemistry*, 6th ed. New York: John Wiley & Sons).

Chlorine reactions may be classified broadly under two types: (i) oxidation-reduction and (ii) substitution reactions. The standard electrode potential for $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$ in aqueous solution is -1.36 V. Some examples of both types are highlighted briefly below:

Chlorine combines with hydrogen forming hydrogen chloride, HCl. The reaction occurs rapidly when exposed to light, involving a photochemical chain initiation step.

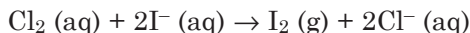


Reactions with most metals yield metal chlorides. Alkali metals are obviously most reactive. With metals that exhibit varying oxidation states, the nature of the product depends on the amount of chlorine. For example, iron reacts with a limited amount of chlorine to produce iron(II) chloride, while in excess chlorine the product is iron(III) chloride:



Among halogens, chlorine can oxidize bromide and iodide ions in solution under acidic conditions, but not fluoride. For example, it can liberate iodine in

acid pH, a reaction widely employed in the iodometric titration to measure residual chlorine in water:



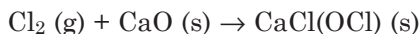
When chlorine is dissolved in a base, the hypochlorous acid, HOCl, is neutralized, forming hypochlorite ion, OCl^- :



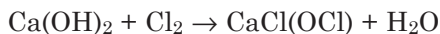
However, in hot basic solution it forms chlorate, ClO_3^- and chloride, Cl^- :



Reaction with lime produces a calcium salt, known as bleaching powder:



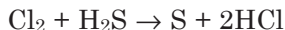
Also, bleaching powder is made by passing Cl_2 gas over slaked lime:



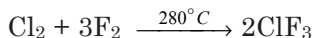
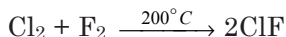
Chlorine readily combines with many nonmetals. Reaction with sulfur yields sulfur dichloride, SCl_2 ; and with phosphorus the products are phosphorus trichloride, PCl_3 and phosphorus pentachloride, PCl_5 .

Chlorine forms carbonyl chloride, COCl with carbon monoxide; sulfuryl chloride SO_2Cl with sulfur dioxide; and chloramines (monochloramine, NH_2Cl , and dichloramine, NHCl_2) with ammonia. Chloramines are often found at trace concentrations in sewage wastewater following chlorine treatment.

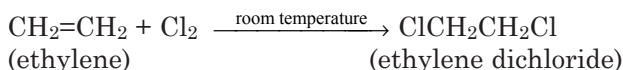
Chlorine oxidizes hydrogen sulfide to sulfur:



Many interhalogen compounds of chlorine with fluorine, bromine and iodine are known. These include ClF , ClF_3 , BrCl , ICl , and ICl_3 .

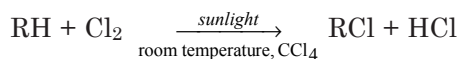


Several classes of organic compounds can react with chlorine. While chlorine adds to an olefinic double bond ($\text{C}=\text{C}$) yielding addition products, reactions with aromatics and saturated hydrocarbons produce substitution products:

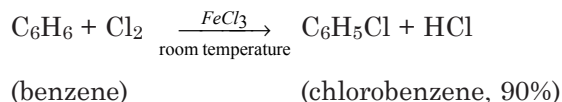


The above reaction is rapid.

With alkanes, substitution occurs producing alkyl chlorides:



The reaction with an alkane, for example, ethane, occurs at room temperature in the presence of UV light. However, substitution can occur in the dark when the gaseous mixture of chlorine and ethane is at 100°C.



Benzene undergoes a substitution reaction yielding 90% chlorobenzene.

Analysis

Chlorine gas may be identified readily by its distinctive color and odor. Its odor is perceptible at 3 ppm concentration in air. Chlorine may be measured in water at low ppm by various titrimetry or colorimetric techniques (APHA, AWWA and WEF. 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington DC: American Public Health Association). In iodometric titrations aqueous samples are acidified with acetic acid followed by addition of potassium iodide. Dissolved chlorine liberates iodine which is titrated with a standard solution of sodium thiosulfate using starch indicator. At the endpoint of titration, the blue color of the starch solution disappears. Alternatively, a standardized solution of a reducing agent, such as thiosulfate or phenylarsine oxide, is added in excess to chlorinated water and the unreacted reductant is then back titrated against a standard solution of iodine or potassium iodate. In amperometric titration, which has a lower detection limit, the free chlorine is titrated against phenyl arsine oxide at a pH between 6.5 and 7.5.

Free and combined chlorine or the total chlorine in water may be measured by titration with ferrous ammonium sulfate using N,N-diethylphenylenediamine (DPD) indicator. Chlorine in aqueous solutions may be measured rapidly using several colorimetric methods that involve addition of various color-forming reagents, and measuring the color intensity using a spectrophotometer or filter photometer. Such reagents include DPD; 3,5-dimethoxy-4-hydroxybenzaldazine (syringaldazine); or 4,4',4''-methylidyne tris(N,N-dimethylaniline) (also known as leucocrystal violet). Several types of chlorine meters are available commercially for rapid *in-situ* colorimetric measurements of chlorine in water.

Hazard

Chlorine is a pungent suffocating gas, exposure to which can cause irritation of the eyes, nose and throat; burning of mouth; coughing; choking; nausea, vomiting; dizziness and respiratory distress. Exposure to 15–20 ppm of chlorine in air can cause irritation and coughing. A 30 minute exposure to

500–800 ppm can be fatal to humans (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons).

Chlorine-hydrogen mixture can explode in the presence of sunlight, heat or a spark. Also, it can explode when mixed with acetylene or diborane at ordinary temperatures, and with ethylene, fluorine, and many hydrocarbons in the presence of heat, spark or catalysts.

CHLORINE DIOXIDE

[10049-04-4]

Formula: ClO_2 ; MW 67.45

Synonyms: chlorine peroxide; chloroperoxyl; Alcide

Uses

Chlorine dioxide is used for bleaching textiles, paper-pulp, cellulose, leather, beeswax, oils, and fats. Other applications are in water treatment processes to kill bacteria, oxidize impurities, and control the taste and odor of water. It also is used to prepare many chlorite salts. Dilute solutions are used as antiseptics.

Physical Properties

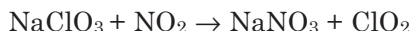
Yellow to red-yellow gas at room temperature; pungent chlorine-like odor; density 9.99 g/L at 11°C; liquefies to a reddish brown liquid at 11°C; liquid density 1.64 g/mL at 0°C; freezes at -59.5°C to red crystals (explodes); soluble in water, decomposes in hot water; soluble in alkalis and H_2SO_4 .

Thermochemical Properties

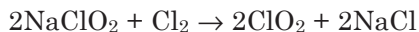
$\Delta H_f^\circ(\text{g})$	24.5 kcal/mol
$\Delta H_f^\circ(\text{aq})$	17.9 kcal/mol
$\Delta G_f^\circ(\text{g})$	28.8 kcal/mol
$S^\circ(\text{g})$	61.4 cal/degree mol
$S^\circ(\text{aq})$	39.4 cal/degree mol
$C_p(\text{g})$	10.0 cal/degree mol

Preparation

Chlorine dioxide is prepared by passing nitrogen dioxide through sodium chlorate packed in a column:



Also, it may be prepared by the reaction of chlorine with sodium chlorite:



Alternatively, it may be obtained by the treatment of sodium chlorate or potassium chlorate with sulfur dioxide and sulfuric acid:



Reactions

In chlorine dioxide, chlorine is in oxidation state +4, which makes the compound highly unstable. The pure compound or its mixture in air at 10% or greater concentrations detonates when exposed to light, or subjected to heat or a spark. The compound also decomposes in the dark in the presence of chlorides. In water, it hydrolyzes slightly to chlorous acid, HClO_2 and chloric acid, HClO_3 . However, in hot water it decomposes, forming chloric acid, chlorine and oxygen:



Reaction with sodium hydroxide in the presence of carbonaceous matter and lime produces sodium chlorite.

Being a strong oxidizing agent, its reactions with reducing agents or oxidizable substances can be violent to explosive. Under controlled conditions, it can be combined with many metals to obtain their chlorite salts.

Hazard

Chlorine dioxide explodes violently when exposed to sunlight, heat, dust or sparks. Also, it detonates at concentrations above 10% in air in the presence of light, heat or catalyst. Reactions with organic substances, metal hydrides, sulfur and phosphorus are violent. The gas is highly irritating to eyes, nose, and throat. Inhalation can produce coughing, respiratory distress, and lung congestion.

CHLORINE MONOXIDE

[7791-21-1]

Formula: Cl_2O ; MW 86.905

Synonyms: dichlorine monoxide; dichloroxide; hypochlorous anhydride; dichloromonoxyde

Uses

Chlorine monoxide is used as a selective chlorinating agent.

Physical Properties

Yellowish-brown gas; disagreeable suffocating odor; unstable at room temperature; gas density 3.89 g/L at 0°C; condenses to a reddish brown liquid at 2.2°C; freezes at -20°C; highly soluble in water; also soluble in alkalis, sulfuric acid, and carbon tetrachloride.

Thermochemical Properties

ΔH_f° (g)	19.2 kcal/mol
ΔG_f° (g)	23.4 kcal/mol
S° (g)	63.6 cal/degree mol
C_p	10.85 cal/degree mol

Preparation

Chlorine monoxide is prepared by passing chlorine gas over yellow mercuric oxide. It is stored below -80°C as a liquid or solid.

Reactions

The oxidation state of chlorine is +1. The compound is highly unstable, decomposing to chlorine and oxygen when exposed to light, heat, spark, or under catalytic conditions. It reacts with hot water forming hypochlorous acid:



It oxidizes a number of compounds, undergoing violent decomposition. It reacts with metals under controlled conditions, forming their hypochlorites.

Hazard

Although a nonflammable gas, it reacts explosively with many substances, including organics, metals, metal sulfides, sulfur, phosphorus, nitric oxide, ammonia, carbon disulfide, metal hydrides, and charcoal. It is a severe irritant to the eyes, nose, skin, and respiratory tract. Inhalation of the gas at 100 ppm can be fatal to humans.

CHLORINE TRIFLUORIDE

[7790-91-2]

Formula: ClF_3 ; MW 92.45

Synonym: chlorotrifluoride

Uses

Chlorine trifluoride is used in rocket propellant; incendiaries; and in processing of nuclear reactor fuel. It also is used as a fluorinating agent and as an inhibitor of fluorocarbon polymer pyrolysis.

Physical Properties

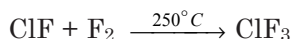
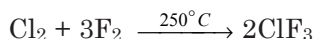
Colorless gas; sweetish but suffocating odor; density of the liquid 1.77 g/mL at 13°C ; condenses to a greenish yellow liquid at 11.75°C ; freezes to a white solid at -76.3°C ; reacts violently with water.

Thermochemical Properties

ΔH_f° (l)	-45.3 kcal/mol
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Preparation

Chlorine trifluoride is obtained by heating chlorine or chlorine monofluoride with fluorine:



The gas is purified by distillation in a special steel apparatus.

Hazard

Although nonflammable, ClF_3 gas is dangerously reactive. It reacts explosively with water and violently with most common substances. Organic materials burst into flame in contact with the liquid. The gas is a severe irritant to the eyes, nose, throat and skin. Inhalation can cause lung damage. The liquid is dangerously corrosive to skin.

CHROMIUM

[7440-47-3]

Symbol: Cr; atomic number 24; atomic weight 51.996; a Group VI-B (Group 6) transition metal; atomic radius 1.27Å; electron configuration $[\text{Ar}]3d^54s^1$; common valences +2, +3 and +6; also oxidation states +4, +5 and 0 are known; isotopes and their abundances: Cr-50 (4.31%), Cr-52 (83.76%), Cr-53 (9.55%), Cr-54 (2.386%).

Occurrences and Uses

Chromium occurs in the minerals chromite, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and crocoite, PbCrO_4 . The element is never found free in nature. Its abundance in earth's crust is estimated in the range 0.01% and its concentration in sea water is 0.3 µg/L. The element was discovered by Vaquelin in 1797.

The most important application of chromium is in the production of steel. High-carbon and other grades of ferro-chromium alloys are added to steel to improve mechanical properties, increase hardening, and enhance corrosion resistance. Chromium also is added to cobalt and nickel-base alloys for the same purpose.

Refractory bricks composed of oxides of magnesium, chromium, aluminum and iron and trace amounts of silica and calcium oxide are used in roofs of open hearths, sidewalls of electric furnaces and vacuum apparatus and copper converters. Such refractories are made in an arc furnace by fusing mixtures of magnesite and chrome ore.

Chromium coatings are applied on the surface of other metals for decorative purposes, to enhance resistance, and to lower the coefficient of friction. Radioactive chromium-51 is used as a tracer in the diagnosis of blood volume.

Physical Properties

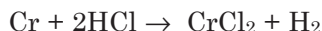
Hard blue-white metal; body-centered cubic crystal; density 7.19 g/cm³; melts at 1,875°C; vaporizes at 2,199°C; electrical resistivity at 20°C, 12.9 microhm-cm; magnetic susceptibility at 20°C, 3.6×10⁻⁶ emu; standard electrode potential 0.71 V (oxidation state 0 to +3).

Reactions

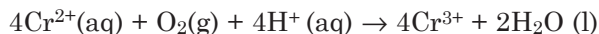
Chromium is oxidized readily in air forming a thin, adherent, transparent coating of Cr₂O₃.

Chromium forms both the chromous (Cr²⁺) and chromic (Cr³⁺) compounds that are highly colored.

Chromium metal reacts readily with dilute acids forming a blue Cr²⁺ (aq) solution with the evolution of hydrogen:



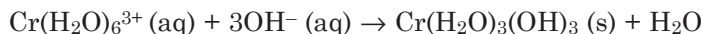
Chromium in metallic form and as Cr²⁺ ion are reducing agents. The Cr²⁺ reduces oxygen within minutes, forming violet Cr³⁺ ion:



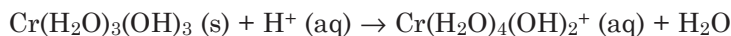
The standard redox potential for the overall reaction is 1.64V.

Cr³⁺ ion forms many stable complex ions. In the aqueous medium, it forms the violet Cr(H₂O)₆³⁺ ion which is slightly basic. Chromium(III) ion is amphoteric, exhibiting both base and acid behavior.

Chromium reaction in an aqueous solution with a base produces a pale blue-violet precipitate having composition: Cr(H₂O)₃(OH)₃.



The above precipitate redissolves in excess base:



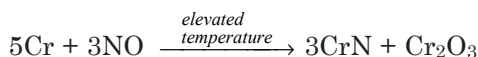
Chromium forms chromium(VI) oxide in which the metal is in +6 oxidation state. In acid medium it yields yellow chromate ion, CrO₄²⁻, and the red-orange dichromate ion, Cr₂O₇²⁻.

Chromium is oxidized in nitric, phosphoric or perchloric acid forming a thin oxide layer on its surface, thus making the metal even more unreactive to dilute acids.

Elemental chromium reacts with anhydrous halogens, hydrogen fluoride, and hydrogen chloride forming the corresponding chromium halides. At elevated temperatures in the range 600 to 700°C, chromium reacts with hydrogen sulfide or sulfur vapor, forming chromium sulfides.

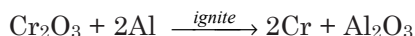
Chromium metal reacts at 600 to 700°C with sulfur dioxide and caustic alkalis. It combines with phosphorus at 800°C. Reaction with ammonia at

850°C produces chromium nitride, CrN. Reaction with nitric oxide forms chromium nitride and chromium oxide.

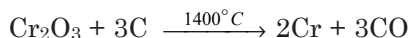


Production

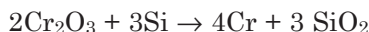
Chromium metal is produced by thermal reduction of chromium(III) oxide, Cr₂O₃ by aluminum, silicon or carbon. The starting material in all these thermal reduction processes are Cr₂O₃ which is obtained from the natural ore chromite after the removal of iron oxide and other impurities. In the aluminum reduction process, the oxide is mixed with Al powder and ignited in a refractory-lined vessel. The heat of reaction is sufficient to sustain the reaction at the required high temperature. Chromium obtained is about 98% pure, containing traces of carbon, sulfur and nitrogen.



The carbon reduction process is carried out at 1,300 to 1,400°C at low pressure in a refractory reactor:



The silicon reduction process is not thermally self-sustaining and, therefore, is done in an electric arc furnace:



Chromium may be produced from high-carbon ferrochrome by electrolytic process. Alternatively, the metal may be obtained by electrolysis of chromic acid, H₂CrO₄.

High-carbon ferrochromium alloys are made by the reduction of chromite ore with carbon in an arc furnace. On the other hand, low-carbon ferrochromium is obtained by silicon reduction of the ore. The carbon content of ferrochromium can be reduced further by heating high-carbon alloys with ground quartzite or by oxidation in vacuum and removal of carbon monoxide formed. Ferrochromium alloys are used in the manufacture of stainless steel.

Analysis

Chromium metal may be analyzed by various instrumental techniques including flame and furnace AA spectrophotometry (at 357.9 nm); ICP emission spectrometry (at 267.72 or 206.15 nm), x-ray fluorescence and x-ray diffraction techniques, neutron activation analysis, and colorimetry.

Chromium metal may be detected in high nanogram to low microgram ranges by these techniques. While AA, ICP, and colorimetric methods require chromium to be brought into aqueous phase, the metal may be analyzed non-destructively in the solid phase by x-ray techniques. ICP-MS technique may

be applied to measure the metal at a much lower detection level.

Toxicity

While chromium metal or trivalent chromium is not very toxic, hexavalent chromium (Cr^{6+}) is carcinogenic and moderately toxic. Cr^{6+} is corrosive to skin and causes denaturation and precipitation of tissue proteins. Inhalation of Cr^{6+} dust or mist can cause perforation of the nasal septum, lung irritation, and congestion of the respiratory passages. Chronic exposure may produce cancer of the respiratory tract.

CHROMIUM(II) CHLORIDE

[10049-05-5]

Formula: CrCl_2 ; MW 122.90; also forms a tetrahydrate, tetraaquochromium dichloride $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2$ [13931-94-7]

Synonym: chromous chloride

Uses

Chromium(II) chloride is used as a reducing agent; as a catalyst in organic reactions; in chromium plating of metals; and as an analytical reagent for the dehalogenation of vic-dihalides. As a reducing agent, it is used to reduce alpha-haloketones to parent ketones, epoxides to olefins, chloroimides to imines, and aromatic aldehydes to corresponding alcohols.

Physical Properties

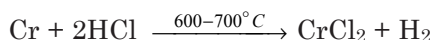
White lustrous needles or fibrous mass; hygroscopic; density 2.88 g/cm^3 ; melts at 814°C ; vaporizes at $1,300^\circ\text{C}$; highly soluble in water, forming blue solution; insoluble in ether. The tetrahydrate occurs in blue hygroscopic crystalline form, that changes to green modification above 38°C ; decomposes to trihydrate at 51°C ; soluble in water.

Thermochemical Properties

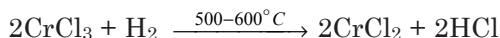
ΔH_f°	-94.50 kcal/mol
ΔG_f°	-85.09 kcal/mol
S°	$27.56 \text{ cal/degree mol}$
C_p	$17.02 \text{ cal/degree mol}$
ΔH_{fus}	7.70 kcal/mol
ΔH_{vap}	47.08 kcal/mol

Preparation

Chromium(II) chloride may be prepared by the reaction of chromium with anhydrous hydrogen chloride at 600 to 700°C :



Also, the compound may be prepared by the reduction of chromium(III) chloride with hydrogen at 500 to 600°C:



An aqueous solution of chromium(II) chloride for organic reduction may be prepared as follows:

Amalgamate zinc by shaking 400 g zinc dust with a solution containing 32g HgCl_2 , 20 mL conc. HCl and 400 mL water. Decant the aqueous phase. To the amalgamated zinc add 800 mL water, 80 mL conc. HCl , and 200 g $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Bubble CO_2 through the solution to agitate it and prevent any possible reoxidation of chromium by air. The solution that turns light blue may be used in organic reduction.

Analysis

Elemental composition: Cr 42.31%, Cl 57.69%. The metal may be analyzed by AA, ICP, or other instrumental techniques. Chloride may be measured by ion chromatography or by using a chloride ion selective electrode. Because of the blue color of its aqueous solution, end point detection in titrimetric methods may be difficult.

CHROMIUM(III) CHLORIDE

[10025-73-7]

Formula: CrCl_3 ; MW 158.35; also forms several hexahydrate isomers, the most common of which is dark green colored *trans*-isomer of dichlorotetraaquo chromium chloride dihydrate, *trans*- $[\text{CrCl}_2(\text{H}_2\text{O})_4\text{Cl}] \cdot 2\text{H}_2\text{O}$ [10064-12-5].

Synonyms: chromic chloride; chromium trichloride; chromium sesquichloride.

Uses

Chromium(III) chloride is used for chromium plating; as textile mordant; in tanning; as a waterproofing agent; and as catalyst for polymerization of olefins.

Physical Properties

Reddish violet crystals; hexagonal plates; density 2.87g/cm^3 ; melts at $1,152^\circ\text{C}$; decomposes at $1,300^\circ\text{C}$; slightly soluble in water. The color of hexahydrates range from light-green to violet; all are hygroscopic; density 1.76g/cm^3 ; soluble in water and ethanol; insoluble in ether; dilute aqueous solutions are violet in color.

Thermochemical Properties

ΔH_f°	-133.01 kcal/mol
ΔG_f°	-116.18 kcal/mol

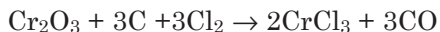
S°	29.40 cal/degree mol
C_p	21.94 cal/degree mol

Preparation

Chromium(III) chloride hexahydrate may be prepared by treating chromium hydroxide with hydrochloric acid:

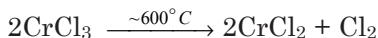


The anhydrous chromium(III) chloride may be obtained by heating the hydrated salt $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ with SOCl_2 and subliming the product in a stream of chlorine at 600°C . Alternatively, the red-violet anhydrous chloride can be obtained by passing chlorine gas over a mixture of chromic oxide and carbon:



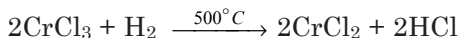
Reactions

Chromium(III) chloride at elevated temperatures decomposes to chromium(II) chloride and chlorine:



Heating with excess chlorine produces vapors of chromium(IV) chloride, CrCl_4 . The tetrahedral tetrachloride is unstable, and occurs only in vapor phase.

When heated with hydrogen, it is reduced to chromium(II) chloride with the formation of hydrogen chloride:



Chromium(III) chloride has very low solubility in pure water. However, it readily dissolves in the presence of Cr^{2+} ion. Reducing agents such as SnCl_2 can "solubilize" CrCl_3 in water. It forms adducts with many donor ligands. For example, with tetrahydrofuran (THF) in the presence of zinc, it forms the violet crystals of the complex $\text{CrCl}_3 \cdot 3\text{THF}$.

Analysis

Elemental composition: Cr 32.84%, Cl 67.16%. Chromium(III) chloride may be solubilized in water by a reducing agent and the aqueous solution may be analyzed for chromium by AA, ICP, or other instrumental techniques. Alternatively, the compound may be digested with nitric acid, brought into aqueous phase, diluted appropriately, and analyzed for the metal as above. The aqueous solution (when a nonchloride reducing agent is used for dissolution of the anhydrous compound in water) may be analyzed for chloride ion by ion chromatography or chloride-selective electrode. The water-soluble hexahydrate may be measured in its aqueous solution as described above.

CHROMIUM HEXACARBONYL

[13007-92-6]

Formula: $\text{Cr}(\text{CO})_6$; MW 220.058; the CO group is bound to Cr atom through C atom; Cr–C bond distance 1.909Å.

Synonym: chromium carbonyl

Uses

Chromium hexacarbonyl is used as an additive to gasoline to increase the octane number; as a catalyst in isomerization and polymerization reactions; and in the preparation of chromium mirror or plate.

Physical Properties

White orthogonal crystal; density 1.77 g/cm³; sublimes at ordinary temperatures; vapor pressure 1 torr at 48°C; decomposes at 130°C; insoluble in water and alcohols; soluble in ether, chloroform and methylene chloride.

Preparation

Chromium hexacarbonyl is prepared by the reaction of anhydrous chromium(III) chloride with carbon monoxide in the presence of a Grignard reagent. A 60% product yield may be obtained at the carbon monoxide pressures of 35 to 70 atm. Other chromium salts may be used with carbon monoxide and Grignard reagent in the preparation. The compound may also be obtained by the reaction of a chromium salt with carbon monoxide in the presence of magnesium in ether or sodium in diglyme.

Reaction

Chromium hexacarbonyl decomposes on strong heating (explodes around 210°C). The product is chromous oxide, CrO. In inert atmosphere the products are chromium and carbon monoxide. It also is decomposed by chlorine and fuming nitric acid. Photochemical decomposition occurs when its solutions are exposed to light.

Some important reactions of chromium hexacarbonyl involve partial or total replacements of CO ligands by organic moieties. For example, with pyridine (py) and other organic bases, in the presence of UV light or heat, it forms various pyridine-carbonyl complexes, such as $(\text{py})\text{Cr}(\text{CO})_5$, $(\text{py})_2\text{Cr}(\text{CO})_4$, $(\text{py})_3\text{Cr}(\text{CO})_3$, etc. With aromatics (ar), it forms complexes of the type, $(\text{ar})\text{Cr}(\text{CO})_3$. Reaction with potassium iodide in diglyme produces a potassium diglyme salt of chromium tetracarbonyl iodide anion. The probable structure of this salt is $[\text{K}(\text{diglyme})_3][\text{Cr}(\text{CO})_4\text{I}]$.

Analysis

Elemental composition: Cr 23.63%, C 32.75%, O 43.62%. A small amount of solid compound may be digested cautiously with nitric acid and the aqueous acid extract may be analyzed for chromium by AA, ICP, or a related tech-

nique. The carbonyl ligand may be determined by thermal decomposition of the compound in an inert atmosphere at temperatures below 180°C followed by the measurement of carbon monoxide by IR, GC–TCD, or GC/MS. Alternatively, the compound may be dissolved in chloroform and analyzed by the above techniques. The characteristic mass ions for GC/MS determination should be 28 for CO and 220 for the molecular ion.

Hazard

Chromium hexacarbonyl is highly toxic by all routes of exposure. The symptoms include headache, dizziness, nausea and vomiting. The LD₅₀(oral) in mice is 150 mg/kg (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons). It explodes upon heating at 210°C.

CHROMIUM(III) HYDROXIDE TRIHYDRATE

[1308-14-1]

Formula: Cr(OH)₃•3H₂O; MW 157.06; occurs only as hydrates

Synonyms: chromic hydroxide; chromic oxide hydrous; chromic oxide gel; chromium hydrate; chromic hydrate.

Uses

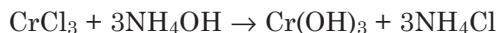
Chromium(III) hydroxide is used as green pigment; as mordant; as a tanning agent; and as a catalyst.

Physical Properties

Bluish-green powder or green gelatinous precipitate; decomposes to chromium(III) oxide on heating; insoluble in water; soluble in dilute mineral acids when freshly prepared, becoming insoluble on aging; soluble in strong alkalis.

Preparation

Chromium(III) hydroxide may be prepared by precipitation from mixing ammonium hydroxide solution with a soluble chromium(III) salt, such as chromium(III) chloride or nitrate:



Analysis

The aqueous solution may be analyzed for chromium by AA or ICP techniques. Chromium(III) may be measured by ion chromatography. Additionally, the compound may be decomposed thermally to chromium(III) oxide, Cr₂O₃, which can be identified by x-ray techniques. Water content of the hydroxide may be measured by gravimetry.

CHROMIUM(III) FLUORIDE

[7788-97-8]

Formula: CrF_3 ; MW 108.99; also forms a trihydrate, triaquochromium trifluoride, $\text{CrF}_3 \cdot 3\text{H}_2\text{O}$ [16671-27-5]; tetrahydrate $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ and nonahydrate $\text{CrF}_3 \cdot 9\text{H}_2\text{O}$ are also known.

Synonyms: chromic fluoride; chromium trifluoride

Uses

Some important uses are in printing and dyeing woollens; mothproofing of woolen materials; metal polishing; coloring marbles; and as a catalyst in halogenation reactions.

Physical Properties

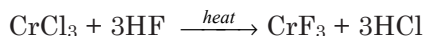
Dark green needles (anhydrous salt) or green hexagonal crystals (trihydrate); density 3.8 g/cm³ (anhydrous fluoride), 2.2 g/cm³ (trihydrate); anhydrous salt melts at 1,100°C and sublimes above this temperature; practically insoluble in water and ethanol (anhydrous salt); trihydrate sparingly soluble in water; soluble in HCl forming a violet solution.

Thermochemical Properties

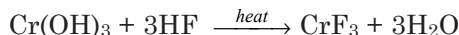
ΔH_f°	-277.0 kcal/mol
ΔG_f°	-260.0 kcal/mol
S°	22.44 cal/degree mol
C_p	18.81 cal/degree mol

Preparation

Chromium(III) fluoride may be prepared by heating chromium trichloride under a stream of hydrogen fluoride:



The compound may be prepared by the reaction of chromium hydroxide with hydrofluoric acid:

**Analysis**

Elemental composition: Cr 47.71%, F 52.29%. A nitric or hydrochloric acid solution of the compound may be analyzed for chromium by various instrumental techniques (see Chromium). The solution may be diluted appropriately and measured for fluoride ion by using a fluoride-selective electrode or by ion chromatography.

CHROMIUM(III) OXIDE

[1308-38-9]

Formula: Cr_2O_3 ; MW 151.99

Synonyms: chromic oxide; chromia; chromium sesquioxide; green cinnabar; chrome green; chrome oxide green; oil green; leaf green; ultramarine green; CI 77288

Uses

Chromium(III) oxide is used as pigment for coloring green on glass and fabrics. Other important applications are in metallurgy; as a component of refractory bricks, abrasives and ceramics; and as a catalyst in hydrogenation, hydrogenolysis and many other organic conversion reactions. It also is used to prepare other chromium salts.

Physical Properties

Green hexagonal crystal system; corundum type structure; density 5.22 g/cm³; melts at 2,330°C; vaporizes above 3,000°C; insoluble in water and alcohol.

Thermochemical Properties

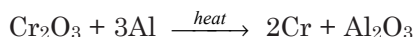
ΔH_f°	-272.4 kcal/mol
ΔG_f°	-252.9 kcal/mol
S°	19.41 cal/degree mol
C_p	28.37 cal/degree mol
ΔH_{fus}	31.07 kcal/mol

Preparation

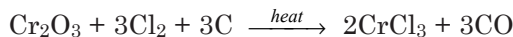
Chromium(III) oxide may be prepared by several methods which include (i) burning the metal in oxygen, (ii) by heating chromium(III) hydroxide, (iii) by heating chromium(VI) oxide, CrO_3 , (iv) thermal decomposition of dry ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, and (v) by heating a mixture of sodium chromate, Na_2CrO_4 or sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$ with sulfur followed by treatment with water to remove the soluble sodium sulfate formed in the reaction.

Reactions

Chromium(III) oxide is amphoteric. Although insoluble in water, it dissolves in acid to produce hydrated chromium ion, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. It dissolves in concentrated alkali to yield chromite ion. When heated with finely divided aluminum or carbon it is reduced to chromium metal:



Heating with chlorine and carbon yields chromium(III) chloride:



Analysis

Elemental composition; Cr 68.43%, O 31.57%. The compound may be identified nondestructively by various x-ray techniques. It may be digested with concentrated nitric acid, the acid extract diluted appropriately and analyzed for chromium by flame or furnace AA or ICP spectrophotometry.

CHROMIUM(VI) OXIDE

[1333-82-0]

Formula: CrO_3 ; MW 99.994

Synonyms: chromium trioxide; chromic anhydride; "chromic acid"

Uses

Chromium(VI) oxide is used for chromium plating; copper stripping; as an oxidizing agent for conversion of secondary alcohols into ketones (Jones oxidation); as a corrosion inhibitor; in purification of oil; and in 'chromic mixtures' for cleaning laboratory glassware.

Physical Properties

Dark-red crystals, flakes or granular powder; bipyramidal prismatic system; density 2.70 g/cm³; melts at 197°C; decomposes on further heating; highly soluble in water, 61.7 g and 67 g/100 mL at 0°C and 100°C, respectively; soluble in sulfuric and nitric acids.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	-140.9 kcal/mol
$\Delta H_f^\circ(\text{g})$	-92.2 kcal/mol
ΔH_{fus}	3.77 kcal/mol

Preparation

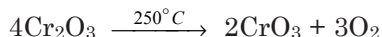
Chromium(VI) oxide is prepared by heating sodium dichromate dihydrate with a slight excess of sulfuric acid in a steel tank or cast iron container:



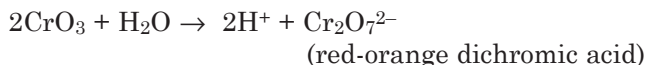
The temperature of the mixture is kept above the melting point of chromium(VI) oxide to evaporate water and separate the top layer of sodium bisulfate from the molten chromium(VI) oxide at the bottom. Temperature control and duration of heating is very crucial in the process. Temperatures over 197°C (melting point), or allowing the molten mass to stand for a longer time, may result in decomposition of the product.

Reactions

Chromium(VI) oxide decomposes to chromium(III) oxide liberating oxygen when heated at 250°C:



The red oxide is the acid anhydride of two acids, namely, chromic acid, H_2CrO_4 or $\text{CrO}_2(\text{OH})_2$ and the dichromic acid $\text{H}_2\text{Cr}_2\text{O}_7$. Both the chromic and dichromic acids exist only in the aqueous solution and have not been isolated from the solution. Dissolution of CrO_3 in water produces H^+ ion along with dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$ as follows:



The aqueous solution of CrO_3 is, therefore, strongly acidic because of this proton release. The $\text{Cr}_2\text{O}_7^{2-}$ ion in the aqueous solution is susceptible to further decomposition, forming chromate ion:

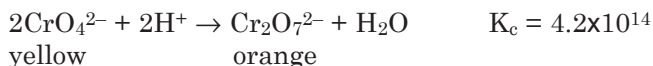


In the above reaction the equilibrium, however, lies far to the left. Therefore the chromium(VI) oxide solution also contains trace amounts of chromate ion, CrO_4^{2-} .

Addition of stoichiometric amounts of caustic soda or caustic potash yields orange dichromate salt which can be crystallized from the solution.

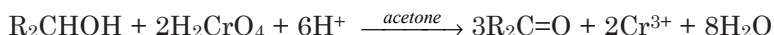


If excess base is added to this solution, it turns yellow, and yellow chromate salt may crystallize out. Thus, as mentioned above, in an aqueous solution of CrO_3 , there is an equilibrium between two Cr^{6+} species, namely, the chromate and dichromate ions:



The addition of base (OH^-) shifts the equilibrium to the left while acidification of the solution shifts the equilibrium to the right in favor of $\text{Cr}_2\text{O}_7^{2-}$. In other color/pH relations, red CrO_3 is acidic, green Cr_2O_3 is amphoteric and the black CrO is basic in nature.

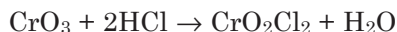
In acid medium chromic acid oxidizes secondary alcohols to ketones:



The reaction usually is carried out in acetone or acetic acid. Chromium is

reduced from +6 to +3 oxidation state.

Reaction with hydrochloric acid yields chromyl chloride:



A similar reaction occurs with HF to yield chromyl fluoride CrO_2F_2 . However, fluorination with F_2 yields the oxohalide, CrOF_4 .

Analysis

Elemental composition: Cr 52.00%, O 48.00%. The compound may be identified from its dark red color. Other color phases are noted above. Chromium may be measured in the aqueous phase by AA, ICP or x-ray techniques, or in the solid phase by x-ray methods. Hexavalent chromium (Cr^{6+}) may be analyzed by ion chromatography. For this, the aqueous sample is adjusted to pH 9 to 9.5 with a concentrated buffer (ammonium sulfate and ammonium hydroxide mixture) and mixed into the eluent stream of the buffer. Cr^{6+} is separated from Cr^{3+} on a column, and derivatized with an azide dye as a colored product measured at 530 nm, which is identified from its retention time. (APHA, AWWA, and WEF. 1999. *Standard Methods for The Examination of Water and Wastewater*, 20th ed., Washington, DC: American Public Health Association.)

CHROMIUM(III) SULFATE

[10101-53-8]

Formula: $\text{Cr}_2(\text{SO}_4)_3$; MW 392.16; several hydrates are known; these include the pentadecahydrate $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ and the octadecahydrate $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

Synonym: chromic sulfate

Uses

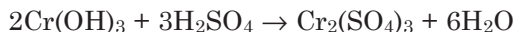
Chromium(III) sulfate is used as the electrolyte for obtaining pure chromium metal. It is used for chrome plating of other metals for protective and decorative purposes. Other important applications of this compound are as a mordant in the textile industry; in tanning leather; to dissolve gelatin; to impart green color to paints, varnishes, inks, and ceramic glazes; and as a catalyst.

Physical Properties

Reddish-brown hexagonal crystal; the pentadecahydrate is a dark green amorphous substance while the octadecahydrate is a violet cubic crystal; the densities are 3.10 g/cm^3 (the anhydrous salt), 1.87 g/cm^3 (pentadecahydrate), 1.709 g/cm^3 (octadecahydrate); the anhydrous sulfate is insoluble in water and acids; the hydrate salts are soluble in water; the pentadecahydrate is insoluble in alcohol, but the octadecahydrate dissolves in alcohol.

Preparation

Chromium(III) sulfate is prepared by treating chromium(III) hydroxide with sulfuric acid followed by crystallization:

**Analysis**

Elemental composition: Cr 26.72%; S 24.52%, O 48.95%. Chromium may be analyzed in the acid extract of the salt by various instrumentation techniques (see Chromium).

CHROMYL CHLORIDE

[14977-61-8]

Formula: CrO_2Cl_2 ; MW 154.90; tetrahedral structure, Cr=O bond distance 1.581 Å and Cr–Cl bond distance 2.126 Å.

Synonyms: chromium dioxychloride; dichlorodioxochromium; chlorochromic anhydride.

Uses

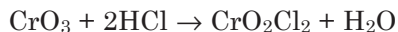
Chromyl chloride is used in many organic synthetic reactions including oxidation and chlorination. It also is used as a catalyst in olefin polymerization; in the preparation of chromium complexes; and as a solvent for chromic anhydride.

Physical Properties

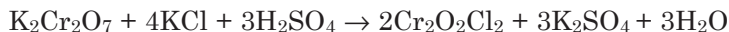
Dark red, fuming liquid; reddish yellow vapors; musty buring odor; density 1.91 g/mL; freezes at -96.5°C ; boils at 117°C ; reacts with water; soluble in chloroform, carbon tetrachloride, benzene, carbon disulfide and nitrobenzene.

Preparation

Chromyl chloride is prepared by reacting chromium(III) chloride with hydrochloric acid:



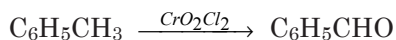
Also, it may be prepared by warming potassium dichromate with potassium chloride in concentrated sulfuric acid:

**Reactions**

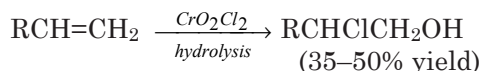
Chromyl chloride reacts with water, hydrolyzing to CrO_4^{2-} and HCl. The compound is sensitive to light but stable in the dark.

Chromyl chloride is a powerful oxidizing agent employed in organic syn-

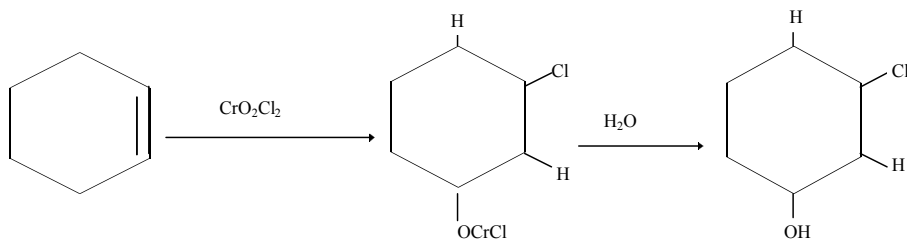
thesis. It oxidizes toluene to benzaldehyde. The reaction is catalyzed by trace olefin.



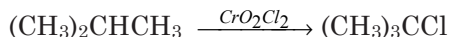
It reacts with olefins forming their chromyl chloride derivatives which on hydrolysis yield chloroalcohols (chlorohydrins) that are mostly the β -chloro-primary alcohols:



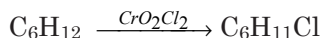
Reaction with cyclohexene yields a trans- β -chlorohydrin:



Chromyl chloride also oxidizes saturated hydrocarbons. For example, it oxidizes isobutane to tert-butyl chloride:



and cyclohexane to chlorocyclohexane:



Analysis

Elemental composition: Cr 33.57%, Cl 45.77%, O 20.66%. A trace amount may be dissolved in a suitable organic solvent and identified and measured quantitatively by GC-FID, GC-ECD, or by mass spectroscopy. For GC-ECD determination, use a nonchlorinated solvent. Chromium may be determined by AA or ICP techniques following thorough digestion in nitric acid.

Hazard

Chromyl chloride reacts violently with alcohol, ammonia, and turpentine, igniting these liquids. Reactions with other oxidizable substances can be violent. The liquid is corrosive and possibly a poison. Skin contact can cause blisters. Exposure to its vapors causes severe irritation of the eyes, nose, and respiratory tract. Prolonged or excessive inhalation can cause death.

COBALT

[7440-48-4]

Symbol: Co; atomic number 27; atomic weight 58.933; a transition metal, Group VIII (Group 9) element; electron configuration $[\text{Ar}]3d^74s^2$; valence +2 and +3; also valences 0, +1, +4, and +5 are known; natural isotopes Co-59 (99.8%) and Co-57 (0.2%); radioactive isotope Co-60.

Occurrence and Uses

Cobalt has been in use as a coloring agent for glass since ancient times. The metal was isolated by Brandt in 1735 and confirmed as an element by Bergman in 1780. Cobalt is widely distributed in nature, but in small concentrations. Its concentration in the earth's crust is estimated to be about 0.0025% and in the sea water is about 0.02 $\mu\text{g/L}$. Cobalt minerals with their chemical formula and CAS Registry numbers are tabulated below:

Mineral	CAS Registry	Chemical Formula	%
cobaltite	[1303-15-7]	CoAsS_3	35.5
carrolite	[12285-42-6]	CuCo_2S_4	38.7
cattierite	[12017-06-0]	$\text{CoS}_2(\text{Co},\text{Ni})\text{S}_2$	-----
linnaeite	[1308-08-3]	Co_3S_4	48.7
siegenite	[12174-56-0]	$(\text{Co},\text{Ni})_3\text{S}_4$	26.0
erythrite	[149-32-6]	$3\text{CoO} \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$	29.5
heterogenite	[12323-83-0]	$\text{CuO} \cdot 2\text{Co}_2\text{O}_3 \cdot 6\text{H}_2\text{O}^*$	57.0
asbolite	[12413-71-7]	$\text{CoO} \cdot 2\text{MnO}_2 \cdot 4\text{H}_2\text{O}$	-----
safflorite	[12044-43-8]	CoAs_2 (orthogonal)	28.2
smaltite	[12044-42-1]	CoAs_2 (cubic), $(\text{Co}, \text{Ni})\text{As}_3$	28.2
skutterudite	[12196-91-7]	$\text{CoAs}_3(\text{Co},\text{Ni})\text{As}_3$	20.8

* The ore contains varying waters of crystallization.

Most cobalt found on earth is diffused into the rocks. It also is found in coal and soils, and at trace concentrations in animals and plants. It is an essential element for plants and animals (as vitamin B12). Its absence in animals can cause retarded growth, anemia and loss of appetite. The element has been detected in meteorites and in the atmospheres of the sun and other stars.

The most important use of cobalt is in the manufacture of various wear-resistant and superalloys. Its alloys have shown high resistance to corrosion and oxidation at high temperatures. They are used in machine components. Also, certain alloys are used in desulfurization and liquefaction of coal and hydrocracking of crude oil shale. Cobalt catalysts are used in many industrial processes. Several cobalt salts have wide commercial applications (see individual salts). Cobalt oxide is used in glass to impart pink or blue color. Radioactive cobalt-60 is used in radiography and sterilization of food.

Physical Properties

Silvery-white metal; occurs in two allotropic modifications over a wide

range of temperatures—the crystalline closed-packed-hexagonal form is known as alpha form and a face-centered cubic form is the beta (or gamma) form. The alpha form predominates at temperatures up to 417°C and transforms to beta allotrope above this temperature; density 8.86 g/cm³; cast hardness (Brinell) 124; melts at 1,493°C; vaporizes at 2,927°C; Curie temperature 1,121°C; electrical resistivity 5.6 microhm-cm at 0°C; Young's modulus 211 Gpa (3.06x10⁷psi); Poisson's ratio 0.32; soluble in dilute acids.

Thermochemical Properties

$\Delta H_f^\circ(\text{cry})$	0.0
$S^\circ(\text{cry})$	7.14 cal/degree mol
$C_p(\text{cry})$	5.93 cal/degree mol
$\Delta H_f^\circ(\text{g})$	101.51 kcal/mol
$\Delta G_f^\circ(\text{g})$	90.89 kcal/mol
$S^\circ(\text{g})$	42.90 cal/degree mol
ΔH_{fus}	65.73 kcal/mol
Coeff. linear expansion, 40°C	1.336x10 ⁻⁵ /°C

Production

Cobalt is obtained from its ores, which are mostly sulfide, arsenic sulfide or oxide in nature. The finely ground ore is subjected to multistep processing, depending on the chemical nature of the ore.

When the sulfide ore carrollite, $\text{CuS} \cdot \text{Co}_2\text{S}_3$, is the starting material, first sulfides are separated by flotation with frothers. Various flotation processes are applied. The products are then treated with dilute sulfuric acid producing a solution known as copper-cobalt concentrate. This solution is then electrolyzed to remove copper. After the removal of copper, the solution is treated with calcium hydroxide to precipitate cobalt as hydroxide. Cobalt hydroxide is filtered out and separated from other impurities. Pure cobalt hydroxide then is dissolved in sulfuric acid and the solution is again electrolyzed. Electrolysis deposits metallic cobalt on the cathode.

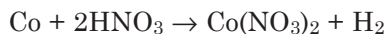
Production of cobalt in general is based on various physical and chemical processes that include magnetic separation (for arsenic sulfide ores), sulfatizing roasting (for sulfide ores), ammoniacal leaching, catalytic reduction, and electrolysis.

Finely divided cobalt particles can be prepared by reduction of cobalt(II) chloride by lithium naphthalenide in glyme.

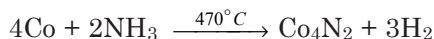
Reactions

Finely divided cobalt is pyrophoric. But the lump metal is stable in air at ordinary temperatures. It is oxidized on heating at 300°C to cobalt oxide.

Reactions with dilute mineral acids yield the corresponding Co^{2+} salts. With hydrochloric acid the reaction is slow. The metal liberates hydrogen from dilute mineral acids:



Cobalt combines with halogens at ordinary temperatures to form their corresponding halides. It reacts with ammonia gas at 470°C to form cobalt nitride, which decomposes at 600°C.



Also it combines with other nonmetals on heating to yield the corresponding binary compounds. With sulfur and phosphorus, cobalt forms sulfides CoS and Co₂S₃ and phosphide Co₂P, respectively. Also, two other cobalt sulfides of stoichiometric compositions, CoS₂ and Co₃S₄ are known. With antimony and arsenic, several antimonides and arsenides are formed. Three antimonides with formulas CoSb, CoSb₂, and CoSb₃ have been reported. Three cobalt arsenides, CoAs, CoAs₂, and CoAs₃ are also known. Cobalt also combines with carbon at elevated temperatures to form carbides of various compositions, namely Co₃C, Co₂C and CoC₂ obtained by dissolution of cobalt in the solid solution. The carbide Co₃C is the primary product when the metal is heated above 1,300°C with carbon in steel containers. When heated with carbon monoxide above 225°C, the carbide Co₂C is readily obtained with deposition of elemental carbon. However, when the metal is in a finely divided state and heated with carbon monoxide at 200°C under pressure (100atm), the product is dicobalt octacarbonyl, Co₂(CO)₈.

When hydrogen sulfide is passed through an ammoniacal or alkaline cobalt solution, a black precipitate of cobalt(II) sulfide, CoS forms.

Cobalt in its trivalent state forms many stable complexes in solution. In these complexes, the coordination number of Co³⁺ is six. The Co²⁺ ion also forms complexes where the coordination number is four. Several complexes of both the trivalent and divalent ions with ammonia, amines, ethylene diamine, cyanide, halogens and sulfur ligands are known (see also Cobalt Complexes).

Analysis

The element may be analyzed in aqueous acidified phase by flame and furnace atomic absorption, ICP emission and ICP-MS spectroscopic methods. Also, at trace concentrations the element may be measured by x-ray fluorescence and neutron activation analysis. Wavelength for AA measurement is 240.7 nm and for ICP analysis is 228.62 nm.

Hazard

In finely powdered form, cobalt ignites spontaneously in air. Reactions with acetylene and bromine pentafluoride proceed to incandescence and can become violent. The metal is moderately toxic by ingestion. Inhalation of dusts can damage lungs. Skin contact with powdered material can cause dermatitis.

COBALT(II) ACETATE

[71-48-7]

Formula: Co(C₂H₃O₂)₂·4H₂O; MW 177.02; the commercial product is manufactured and sold in the tetrahydrate form of the compound,

234 COBALT(II) CARBONATE

$\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ [6147-53-1], MW 249.08

Synonym: cobaltous acetate

Uses

Cobalt(II) acetate is used for bleaching and drying varnishes and laquers. Other applications are: as a foam stabilizer for beverages; in sympathetic inks; as a mineral supplement in animal feed; and as a catalyst for oxidation. It also is used in aluminum anodizing solutions.

Physical Properties (Tetrahydrate)

Red-to-violet monoclinic crystals (anhydrous acetate is light pink in color); density 1.705 g/cm³; becomes anhydrous when heated at 140°C; soluble in water, alcohols and acids.

Preparation

Cobalt(II) acetate is prepared by dissolving cobalt(II) carbonate or hydroxide in dilute acetic acid, followed by crystallization. Also, it may be prepared by oxidation of dicobalt octacarbonyl in the presence of acetic acid.

Analysis

Elemental composition (tetrahydrate salt): Co 23.66%, C 19.29%, H 5.67%, O 51.39%. The aqueous solution may be analyzed for cobalt by various instrumental techniques (see Cobalt). The water of crystallization may be measured by gravimetry under controlled heating at 140°C.

COBALT(II) CARBONATE

[513-79-1]

Formula: CoCO_3 ; MW 118.94; also forms a hexahydrate, $\text{CoCO}_3 \cdot 6\text{H}_2\text{O}$

Synonym: cobaltous carbonate

Uses

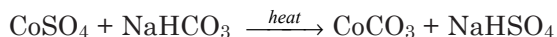
The compound occurs in nature as the mineral cobalt spar or sphaerocobaltite. It is used in ceramics; in cobalt pigments; as a catalyst; as a temperature indicator; and in the preparation of other cobalt(II) salts. It also is added to soil to provide nutritional supplement in forage for cattle.

Physical Properties

Pink rhombohedral crystals; refractive index 1.855; density 4.13 g/cm³; decomposes on heating; insoluble in water and ethanol; soluble in acids.

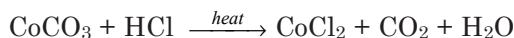
Preparation

Cobalt(II) carbonate is prepared by heating cobaltous sulfate, cobaltous chloride or any Co^{2+} salt with sodium bicarbonate in solution:



Reactions

Cobalt(II) carbonate dissolves in concentrated HCl or HNO₃ when heated, evolving CO₂:



It is oxidized by air or weak oxidizing agents, forming cobalt(III) carbonate, Co₂(CO₃)₃. It decomposes on heating, forming the oxides of cobalt with the evolution of CO₂.

Analysis

Elemental composition: Co 49.55% C 10.10%, O 40.35%. Analysis of cobalt may be performed by digesting a measured amount of the compound in hot nitric acid followed by appropriate dilution and measurement by AA, ICP or other instrumental technique (see Cobalt). Also, treatment with hot acid liberates CO₂ (with effervescence) which turns lime water milky. The CO₂ may be analyzed by several tests (see Carbon Dioxide).

Toxicity

The compound is moderately toxic by ingestion. (Lewis (Sr.), R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold.)

LD₅₀ oral (rat): 640 mg/kg

COBALT CARBONATE, BASIC

[12602-23-2]

Formula: Co₅(OH)₆(CO₃)₂ or 2CoCO₃ · 3Co(OH)₂ · H₂O; MW 516.73

Synonyms: cobalt carbonate hydroxide; cobaltous carbonate basic; basic cobalt carbonate

Uses

The cobalt carbonate basic salt is the commercially-used cobalt carbonate. It is used primarily for manufacturing cobalt pigments. It also is used to prepare cobalt(II) oxide and other cobalt salts.

Physical Properties

Red violet crystal; insoluble in water; decomposes in hot water; soluble in dilute acids and ammonia.

Preparation

The basic carbonate is prepared by adding a solution of sodium carbonate to a cobalt(II) acetate or other Co²⁺ salt solution. The precipitate is filtered and dried.

Analysis

Elemental composition: Co 57.02% , C 4.65% , H 1.17% , O 37.16%. The compound is dissolved in dilute nitric acid and analyzed for cobalt (see Cobalt).

COBALT(II) CHLORIDE

[7646-79-9]

Formula: CoCl_2 ; MW 129.84; also forms dihydrate $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ [16544-92-6] and hexahydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ [7791-13-1]

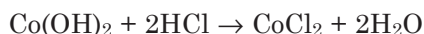
Synonym: cobaltous chloride

Uses

Cobalt(II) chloride has several applications. It is used in hygrometers; as a humidity indicator; as a temperature indicator in grinding; as a foam stabilizer in beer; in invisible ink; for painting on glass; in electroplating; and a catalyst in Grignard reactions, promoting coupling with an organic halide. It also is used to prepare several other cobalt salts; and in the manufacture of synthetic vitamin B12.

Preparation

Cobalt(II) chloride is prepared by the action of cobalt metal or its oxide, hydroxide, or carbonate with hydrochloric acid:



The solution on concentration and cooling forms crystals of hexahydrate which on heating with SOCl_2 dehydrates to anhydrous cobalt(II) chloride. Alternatively, the hexahydrate may be converted to anhydrous CoCl_2 by dehydration in a stream of hydrogen chloride and dried in vacuum at 100–150°C. The anhydrous compound also may be obtained by passing chlorine over cobalt powder.

Physical Properties

Blue leaflets; turns pink in moist air; hygroscopic; the dihydrate is violet blue crystal; the hexahydrate is pink monoclinic crystal; density 3.36, 2.48 and 1.92 g/cm³ for anhydrous salt, dihydrate and hexahydrate, respectively; anhydrous salt melts at 740°C and vaporizes at 1,049°C; vapor pressure 60 torr at 801°C; the hexahydrate decomposes at 87°C; the anhydrous salt and the hydrates are all soluble in water, ethanol, acetone, and ether; the solubility of hydrates in water is greater than the anhydrous salt.

Thermochemical Properties

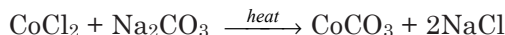
ΔH_f°	−74.69 kcal/mol
ΔG_f°	−64.48 kcal/mol
S°	26.10 cal/degree mol
C_p	18.76 cal/degree mol

$$\Delta H_{\text{fus}}$$

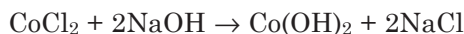
$$10.76 \text{ kcal/mol}$$

Reactions

Cobalt(II) chloride undergoes many double decomposition reactions in aqueous solution to produce precipitates of insoluble cobalt salts. For example, heating its solution with sodium carbonate yields cobalt(II) carbonate:



Reaction with alkali hydroxide produces cobalt(II) hydroxide:



Reaction with ammonium hydrogen phosphate yields cobalt(II) phosphate:



While cobalt(II) fluoride is the product of the reaction of anhydrous cobalt(II) chloride with hydrofluoric acid, cobalt(III) fluoride is obtained from fluorination of an aqueous solution of cobalt(II) chloride.

Addition of potassium nitrite, KNO_2 to a solution of cobalt(II) chloride yields yellow crystalline potassium hexanitrocobaltate(III), $\text{K}_3\text{Co}(\text{NO}_2)_6$.

Analysis

Elemental composition: Co 45.39%, Cl 54.61%. Aqueous solution of the salt or acid extract may be analyzed for cobalt by AA, ICP, or other instrumental techniques following appropriate dilution. Chloride anion in the aqueous solution may be measured by titration with silver nitrate using potassium chromate indicator, or by ion chromatography, or chloride ion-selective electrode.

Toxicity

The compound is toxic at high doses. Symptoms include chest pain, cutaneous flushing, nausea, vomiting, nerve deafness, and congestive heart failure. The systemic effects in humans from ingestion include anorexia, increased thyroid size, and weight loss (Lewis (Sr.), R. J. 1996. *Sax's Dangerous Properties of Industrial Materials*, 9th ed. New York: Van Nostrand Reinhold). Ingestion of a large amount (30–50 g) could be fatal to children.

COBALT COMPLEXES

Cobalt forms many complexes in both the divalent and trivalent states. While the d^7Co^{2+} ion exhibits a coordination number of four or six in the trivalent state, the d^6Co^{3+} ion mostly exhibits coordination number six. Also, trivalent cobalt forms more stable complexes than Co^{2+} ion, and there are many more of them. The most common donor atom in cobalt complexes is nitrogen,

having ammonia and amines as ligands forming numerous complexes. Many cobalt cyanide complexes are known in which CN^- coordinates to the cobalt ion through the carbon atom. In aquo complexes, water molecules coordinate through the oxygen atom. Sulfur ligands and halide ions also form numerous complexes with both Co^{2+} and Co^{3+} ions.

Cobalt complexes have limited but some notable applications. Pentacyanocobalt(II) ion can activate molecular hydrogen homogeneously in solution and therefore can act as a hydrogenation catalyst for conjugated alkenes. Cobalt ammine chelates exhibit catalytic behavior in hydrolysis of carboxylate esters, phosphate esters, amides, and nitriles. Single crystals of cyanide complex are used in laser studies. Many aquo-halo mixed complexes are used in making invisible or sympathetic inks and color indicators for desiccants. Certain chelators, such as cobalt ethylenediamine complexes, have unusual oxygen-carrying properties. These polyfunctional donor molecules have the ability to readily absorb and release oxygen. They are used as a convenient source of purified oxygen.

Cobalt(II) forms more tetrahedral complexes than any other transition metal ion. Also, because of small energy differences between the tetrahedral and octahedral complexes, often the same ligand forms both types of Co(II) complexes in equilibrium in solutions.

Some examples of Co^{2+} complexes having varying coordination number and geometry, are presented below:

Coordination Number	Shape	Ligand	Structure/Formula	Name of complex ion/neutral complex
4	tetrahedral	H_2O	$[\text{Co}(\text{H}_2\text{O})_4]^{2+}$	tetraaquocobalt(II)
4	tetrahedral	$(\text{Cl}^-, \text{Br}^-, \text{I}^-)$	$[\text{Co X}_4]^{2-}$	tetrahalocobalt(II)
4	tetrahedral	SCN^-	$[\text{Co}(\text{SCN})_4]^{2-}$	tetrathiocyanato cobalt(II)
4	tetrahedral	$\text{Cl}^-, \text{H}_2\text{O}$	$[\text{Co}(\text{H}_2\text{O})_2\text{Cl}_2]$	diaquodichlorocobalt(II)
4	tetrahedral	N_3^-	$[\text{Co}(\text{N}_3)_4]^{2-}$	tetraazido cobalt(II)
5	tetrahedral	N-methyl salicylaldimine	a dimer	bis(N-methyl salicylaldiminato)cobalt (II)
6	tetrahedral	acetylacetonate	a tetramer $\text{Co}(\text{acac})_2$	bis(acetylacetonato)cobalt (II)
4	planar	dimethylglyoxime	$\text{Co}(\text{dmg})_2$	bis(dimethylglyoximate)cobalt (II)
4	planar	dithioacetylacetonate	$\text{Co}(\text{dtacac})_2$	bis(dithioacetylacetonato)cobalt(II)
4	planar	salicylaldehyde	$\text{Co}(\text{Salen})_2$	bis(salicylaldehyde ethylenediamine) cobalt(II)
4	planar	porphyrin	$\text{Co}(\text{porph})_2$	bis(porphyrine)cobalt(II)
4 or 6	planar/distorted	ethylenediamine	$[\text{Co}(\text{en})_2]$	bis(ethylenediamino) cobalt(II)
	octahedral	accompanies with an anion	$(\text{AgI}_2)_2$	disilver diiodide
6	octahedral	dimethyl sulfoxide	$[\text{Co}(\text{DMSO})_6]^{2+}$ (the ligand bound through O atom)	hexakis(dimethyl sulfoxide)cobalt(II)
6	octahedral	$\text{CN}^-, \text{H}_2\text{O}$	$[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$	pentacyanoaquocobalt(II)
6	octahedral	SCN^-	$[\text{Co}(\text{SCN})_6]^{2+}$	hexathiocyanatocobalt(II)
5	triangular bipyramidal	trialkyl/aryl phosphines, halide ions, CN^-	$\text{CoBr}_2(\text{PMe}_3)_3$ $\text{Co}(\text{CN})_2(\text{PMe}_2\text{Ph})_3$	dibromotris(trimethyl phosphine)cobalt(II) dicyanotris(dimethylphenyl phosphine)cobalt(II)